

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



D3

(11)

EP 1 319 686 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.06.2003 Bulletin 2003/25

(51) Int Cl.⁷: **C08L 23/06, C08L 23/08,
C08K 3/22, C08L 23/26,
C08L 23/02, H01B 3/44**

(21) Application number: **02293108.3**

(22) Date of filing: **16.12.2002**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SI SK TR**
Designated Extension States:
AL LT LV MK RO

(72) Inventors:
• **Sato, Masashi
1-14 Nishisuehiro-cho Yokkaichi-ken, Mie (JP)**
• **Matsumoto, Shinichi
1-14 Nishisuehiro-cho Yokkaichi-ken, Mie (JP)**

(30) Priority: **17.12.2001 JP 2001382711**

(74) Representative: **Uchida, Kenji et al
S.A. Fedit-Loriot et Autres Conseils en Propriété
Industrielle,
38, avenue Hoche
75008 Paris (FR)**

(71) Applicant: **Sumitomo Wiring Systems, Ltd.
Yokkaichi-City, Mie, 510-8503 (JP)**

(54) **Wear resistant, flame-retardant composition and electric cable covered with said composition**

(57) The present invention relates to a resin composition comprising: (a) 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least 0.930; (b1) 5 to 65 parts by mass of olefin type polymer containing intra molecular oxygen atoms; (c) 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of (c1) acid modified olefin polymers containing

intra-molecular oxygen atoms, (c2) acid modified styrene type thermoplastic elastomers, (c3) acid-modified polyethylenes having a density of about 0.920 at the most, and (c4) acid modified rubbers, with the proviso that the total of components (a), (b1) and (c) represents 100 parts by mass; and (d) 30 to 250 parts by mass of metal hydroxide.

Description

[0001] The present invention relates to a wear resistant, flame-retardant material composition and to an electric cable or wire covered with a material containing such a composition. This type of protected electric cable or wire is used, for example, in automotive vehicles.

[0002] Polyvinyl chloride has been widely used as a coating material for electrical cables or wires used in vehicles, owing to its excellent mechanical strength, facility with which it can be extruded around an electric cable, its excellent flexibility and paintability, as well as its low cost.

[0003] However, because of recent environmental measures, manufacturing of parts for vehicles, including coatings of electrical wires used in vehicles, has started to use halogen free (polymer) materials instead of polyvinyl chloride.

[0004] A halogen free resin composition containing a polyolefin as a base polymer and metal hydroxides as flame retardants is well known (see JP-A-7-176219 and JP-A-7-78518). This composition is a wear resistant resin composition and has the advantage of not producing toxic gas such as halogen gas when burning.

[0005] However, it is necessary to add large amounts of metal hydroxides to make this composition sufficiently flame retardant to yield a self extinguishing property. When adding such large amounts of metal hydroxides, the mechanical strength of the composition, such as its wear resistance and tensile strength falls dramatically. To prevent such lowering of mechanical strength, it has been suggested to raise the amount of propylene having a relatively high hardness and the amount of polypropylene having a high density. However, in this case, the flexibility of the protected electric cable or wire is then lowered and the manufacturability thereof is also lowered.

[0006] JP-A-6-290638 discloses a resin composition containing metal hydroxides used for insulating electrical wires. This composition contains polypropylene as main component (more than 80%). The other components of this composition are copolymers of styrene and polyethylene modified by acid anhydrides.

[0007] US-5561185 discloses as a resin composition containing metal hydroxides, used for protecting electrical wires, a resin composition containing :

(a) 40 to 88.5% by mass (or by weight) of a polypropylene type resin containing at least 50% by mass of ethylene-propylene random copolymers ;

(b) 1.5 to 30% by mass of polyethylene modified by an unsaturated carboxylic acid or derivatives thereof (e.g. maleic anhydride); and

(c) 10 to 48% by mass of ethylene type copolymer, typically ethylene / vinyl acetate copolymer.

[0008] US-5180889 discloses a resin composition containing metal hydroxides as a coating for the conductor of a crash resistant cable. This composition contains :

a) ethylene / α olefin copolymer having a low density ;

b) a system of styrene - ethylene - butylenes - styrene tri-block copolymer - elastomer, preferably modified by maleic anhydride ; and

c) optionally, a shock-resistant propylene copolymer or polypropylene.

[0009] It has been proposed to improve the heat resistance of the resin composition used for electrical wire insulation by cross-linking the resin composition.

[0010] JP-A-8-161942 proposes to coat electrical wires with a resin composition containing an ethylene-vinyl acetate copolymer (EVA), ethylene-ethyl acrylate (EEA) and metal hydrates, and to cross-link this composition using electron beam irradiation.

[0011] JP-A-2000-294039 proposes to cross-link a composition containing ethylene type polymer(s) and maleic anhydride modified polyolefins.

[0012] The compositions obtained by cross-linking a resin composition containing as a base an ethylene type polymer have excellent heat resistance but insufficient wear resistance.

[0013] JP-A-2000-86830 discloses a composition obtained by cross-linking a resin composition containing polyolefin type elastomers, metal hydroxides and a coupling-agent surface treated potassium titanate.

[0014] JP-A-2000-336215 discloses a resin composition containing a polyolefin type resin prepared with magnesium hydroxide or aluminium hydroxide whose surface is treated, silicone powder and a cross-linking accelerator. This composition is also cross-linked.

[0015] Such compositions have an improved tensile and mechanical strength, but a poor flexibility and formability.

[0016] One purpose of the present invention is to provide a flame retardant resin composition containing metal hydroxides which is suitable for coating electrical wires or cables, and which has an extended flame retardant quality, as well as improved wear resistance, flexibility and formability.

[0017] To solve the above-mentioned problem, there is provided a resin composition comprising:

- (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b1) about 5 to 65 parts by mass of olefin type polymer containing intra molecular oxygen atoms;
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

5

- (c1) acid modified olefin polymers containing intra-molecular oxygen atoms;
- (c2) acid modified styrene type thermoplastic elastomers;
- (c3) acid-modified polyethylenes having a density of about 0.920 at the most; and
- (c4) acid modified rubbers,

10 with the proviso that the total of components (a), (b1) and (c) represents 100 parts by mass; and

- (d) about 30 to 250 parts by mass of metal hydroxide.

[0018] Preferably, the resin composition is cross-linked by electron beam irradiation.

[0019] Alternatively, the invention relates to a resin composition comprising:

- (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b2) about 5 to 65 parts by mass of styrene type thermoplastic elastomer; and
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

20 (c1) acid modified olefin type polymers containing intra-molecular oxygen atoms, and
(c2) acid modified styrene type thermoplastic elastomers;
with the proviso that the total of components (a), (b2) and (c) represents 100 parts by mass; and

25

- (d) about 30 to 250 parts by mass of metal hydroxide.

[0020] Preferably, the resin composition is cross-linked by electron beam irradiation.

[0021] The invention further relates to a method for preparing an electrical cable, the method comprising the steps of:

30

- preparing a resin composition comprising:

- (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b1) about 5 to 65 parts by mass of olefin type polymer containing intra molecular oxygen atoms;
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

35 (c1) acid modified olefin polymers containing intra-molecular oxygen atoms;
(c2) acid modified styrene type thermoplastic elastomers;
(c3) acid-modified polyethylenes having a density of about 0.920 at the most; and
(c4) acid modified rubbers,
with the proviso that the total of components (a), (b1) and (c) represents 100 parts by mass; and

40

- (d) about 30 to 250 parts by mass of metal hydroxide; and

45

- coating a conductor element with the resin composition.

[0022] Preferably, the above method further comprises the step of irradiating the resin composition with electron beams.

50 [0023] Alternatively, the invention concerns a method for preparing an electrical cable, the method comprising the steps of:

- preparing a resin composition comprising:

- (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b2) about 5 to 65 parts by mass of styrene type thermoplastic elastomer; and
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

(c1) acid modified olefin type polymers containing intra-molecular oxygen atoms, and
 (c2) acid modified styrene type thermoplastic elastomers;
 with the proviso that the total of components (a), (b2) and (c) represents 100 parts by mass; and

5 - (d) about 30 to 250 parts by mass of metal hydroxide; and
 - coating a conductor element with the resin composition.

10 [0024] Preferably, the above method further comprises the step of irradiating the resin composition with electron beams.

[0025] There is further provided an electrical cable coated with a resin composition comprising:

15 - (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
 - (b1) about 5 to 65 parts by mass of olefin type polymer containing intra molecular oxygen atoms;
 - (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

20 (c1) acid modified olefin polymers containing intra-molecular oxygen atoms;
 (c2) acid modified styrene type thermoplastic elastomers;
 (c3) acid-modified polyethylenes having a density of about 0.920 at the most; and
 (c4) acid modified rubbers,
 with the proviso that the total of components (a), (b1) and (c) represents 100 parts by mass; and

25 - (d) about 30 to 250 parts by mass of metal hydroxide.
 Suitably, the resin composition is further cross-linked by electron beam irradiation.
 There is further provided an electrical cable coated with a resin composition comprising:

30 - (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
 - (b2) about 5 to 65 parts by mass of styrene type thermoplastic elastomer; and
 - (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

35 (c1) acid modified olefin type polymers containing intra-molecular oxygen atoms and
 (c2) acid modified styrene type thermoplastic elastomers;
 with the proviso that the total of components (a), (b2) and (c) represents 100 parts by mass; and

40 - (d) about 30 to 250 parts by mass of metal hydroxide.

[0026] Suitably, the resin composition is further cross-linked by electron beam irradiation.

[0027] The invention also relates to the use of a resin composition defined above for preparing an electrical cable.

[0028] Each component of the composition of the invention is chosen in order to confer, when mixed with the others, a desired property to the resulting material. Explanations regarding each of the components are given hereinafter.

[0029] Component (a) is a polyethylene having a melt flow rate (MFR) of 5g/10 min or less and a density of at least 0.930.

45 [0030] The polyethylene used can be any polyethylene having the above-mentioned density and melt flow rate. However, high density polyethylene or straight-chain low density polyethylene are preferably used.

[0031] When the MFR of polyethylene exceeds 5g/10 min, the formability of the composition is deteriorated.

[0032] The MFR value is measured according to JIS K 6921-2.

50 [0033] Moreover, when the density of the polyethylene is less than 0.930, the hardness of the composition is lowered, and its wear resistance is also lowered.

[0034] The amount of component (a) represents 30 to 90 parts by mass, preferably 30 to 80 parts by mass, in the total of 100 parts by mass consisting of component (a), component (b1) or (b2) and component (c).

[0035] When the amount of component (a) is higher than the upper limit, the flexibility and formability of the composition are lowered. When this amount is lower than the lower limit, the composition has a poor wear resistance.

55 [0036] Examples of olefin polymers (b1) containing intramolecular oxygen atoms include a copolymer of olefins (e.g. ethylene) and unsaturated monomers containing oxygen atoms (e.g. vinyl acetate, ethyl acrylate and ethyl methacrylate). In practice, ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers and ethylene-methyl methacrylate copolymers can be given as examples.

[0037] The styrene type thermoplastic elastomers (b2) may be, for example, thermoplastic copolymers of styrene and olefins (e.g. ethylene or propylene). Practically, styrene-ethylene block copolymers, styrene-ethylene-propylene block copolymers and their hydrogenated derivatives obtained by adding hydrogen atoms in their unsaturated bonds.

5 [0038] The amount of component (b1) or (b2) ranges from 5 to 65 parts by mass, preferably from 10 to 60 parts by mass, in the total of 100 parts by mass consisting of component (a), component (b1) or (b2) and component (c).

[0039] When the amount of component (b1) or (b2) is higher than the above-mentioned upper limit, the wear resistance of the composition is lowered, whilst, when this amount is lower than the above-mentioned lower limit, the flexibility and formability of the composition are lowered.

10 [0040] Examples of acid-modified olefin polymers (c1) containing intramolecular oxygen atoms include polymers which may be obtained by introducing, as acid components, unsaturated carboxylic acids or their derivatives (e.g. anhydrides or esters) into olefin polymers (b1) containing intramolecular oxygen atoms. Typical examples of such unsaturated carboxylic acids or their derivatives include maleic acid, fumaric acid, maleic anhydride, maleic acid monoesters and maleic acid diesters.

15 [0041] The acids can be introduced into the olefin type polymer by grafting or by any direct method (copolymerisation). The amount of acid used for modification or denaturation preferably range from 0.1 to 20 by mass with respect to the mass amount of olefin type polymer.

20 [0042] The acid-modified styrene type thermoplastic elastomers (c2) may be the polymers obtained by introducing, as acid components, unsaturated carboxylic acids or their derivatives (e.g. acid anhydrides or esters) into styrene type thermoplastic elastomers (b2). The types of unsaturated carboxylic acids or their derivatives, the method their introduction and the amount used are the same as described above for the case of component (c1).

25 [0043] The acid-modified polyethylene (c3) having a density of 0.920 or less may be the polymers obtained by introducing, as acid components, unsaturated carboxylic acids or their derivatives (e.g. acid anhydrides or esters) into relatively low density polyethylene (e.g. so-called ultra-low density polyethylene such as ethylene-octene copolymers). The types of unsaturated carboxylic acids or their derivatives, the method of their introduction and the amount used are the same as described above for the case of component (c1).

30 [0044] When the density of acid modified polyethylene is more than 0.920, the hardness of the composition is increased and its flexibility is lowered.

35 [0045] The acid modified rubber (c4) may be obtained, for example, by introducing the above-mentioned unsaturated carboxylic acids or their derivatives into a rubber. Examples of such rubber include ethylene-propylene rubber, ethylene-propylene-diene rubber or the like. The types of unsaturated carboxylic acids or their derivatives, the method of their introduction and the amount used are the same as described above for the case of component (c1).

40 [0046] The amount of component (c) represents from 5 to 40 parts by mass, preferably 10 to 40 parts by mass, in the total of 100 parts by mass consisting of component (a), component (b1) or (b2) and component (c).

45 [0047] When the amount of component (c) is greater than the above-mentioned upper limit, the wear resistance of the composition is lowered. Conversely, when its amount is less than the above-mentioned lower limit, the flexibility and formability of the composition tends to decrease.

50 [0048] Examples of metal hydroxides (d) include magnesium hydroxide, aluminium hydroxide, and the like. Metal hydroxide particles may not be specifically treated. However, the surface may also be treated with a surface treatment agent such as coupling agents, in particular, silane coupling agents (e.g. amino silane coupling agent, vinyl silane coupling agent, epoxy silane coupling agent, methacryloxy silane coupling agent) or optionally higher fatty acids (e.g. stearic acid, oleic acid or the like).

55 [0049] A silane coupling agent typically contains a Si-O bond which can form a bond with hydroxides. Amongst metal hydroxides, a preferred compound is magnesium hydroxide or aluminium hydroxide whose surface is treated with a coupling agent, preferably a silane coupling agent, in particular an aminosilane coupling agent.

[0050] The particles of metal hydroxides may not be pre-treated with a coupling agent. Instead, they may be mixed directly with a resin, then supplemented with a coupling agent, according to a method called "integral blending".

[0051] The amount of metal hydroxide usually represents from 30 to 250 parts by mass, preferably from 50 to 200 parts by mass, the total of component (a), component (b1) or (b2) and component (c) representing 100 parts by mass.

55 [0052] Any known additive may be added into the composition in such an amount that does not damage preferable characteristics of the composition. Examples of the above additives include those usually added into olefin type resins such as heat stabilisers (e.g. oxidation-preventing agents), metal-inactivating agents (copper-pollution preventing agents), lubricants (fatty acids, fatty acid amides, metallic soaps, hydrocarbons e.g. wax, esters, silicone type lubricants), light stabilisers, core-forming agents, electrification-preventing agents, colorants, flame retardant adjuvants, (e.g. zinc borate, silicone type flame retardant, nitrogen type retardant), coupling agents (e.g. silane type coupler, titanate type coupler), softening agents (e.g. process oils), cross-linking adjuvant agents (poly functional monomers and the like).

[0053] The resin composition of the invention may be prepared by mixing and/or kneading the components cited above according to any known method.

[0054] The resin composition of the invention may be cross-linked according to any known method e.g. electron beam irradiation.

[0055] The resin composition of the present invention may be used for coating electrical cables, in particular electrical cables for vehicles according to any known method.

5 [0056] The above, and the other features and advantages of the present invention will be made apparent from the following description of the preferred examples, given as non-limiting examples, with references to the following Examples and Comparative Examples.,

Examples 1 to 10 and Comparative Examples 1 to 9

10 [0057] The components shown in Tables 1 to 4 were mixed together in the amounts (parts by mass) indicated therein, kneaded in a temperature range of 180°C to 260°C, and extruded into pellets by a two-axis extruder. The pellets were dried and extruded and shaped around a conductor element (7/0.30) having a cross section of 0.5 mm², so as to yield a coating of 0.28 mm thick. The coated resin composition was then cross-linked by electron beam irradiation.

15 [0058] The extrusion-shaping was performed using a nipple and dies respectively having a diameter of about 0.93 mm and about 1.45 mm. The extrusion temperatures for the dies and cylinder were respectively about 180°C to about 250°C and about 160°C to about 240°C. The extrusion line speed was 100m/min.

[0059] The electron beam irradiation conditions were as follows.

20 Device : EPS-750 KV
Irradiation intensity : 120KGy

[0060] The following properties of the coated electrical cables obtained in Examples 1 to 10 and Comparative Examples 1 to 9 were evaluated.

25 Flexibility :

[0061] The flexibility was evaluated on the basis of resistance feeling, when the electrical cable was bent manually.

30 Wear resistance and flame retardant quality

[0062] Wear resistance and flame retardant quality were measured according to Standards JASO D 611. As to wear resistance, the results were considered good when the minimum value among 3 samples tested was more than 150 times.

35 Formability

[0063] The formability was evaluated by observing whether or not whiskers were formed when coatings were peeled at the end portion of electrical cables. The results are shown in Tables 1 to 4

40 Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
HDPE 1)	65	50	65	30	40
LLDPE 2)					
EVA 3)	30	10		65	30
EEA 4)			5		
MAH-EVA 5)	5	40	30		30
MAH-EEA 6)				5	
magnesium hydroxide ⁷⁾	100	120	100	250	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	2	4	
total	205	225	203	355	131

Table 1 (continued)

	Example 1	Example 2	Example 3	Example 4	Example 5
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

10

Table 2

	Example 6	Example 7	Example 8	Example 9	Example 10
HDPE ¹⁾		50	50	70	40
LLDPE ²⁾	90				
EVA ³⁾	5	30		10	40
EEA ⁴⁾			30		
MAH-EVA ⁵⁾	5	20	20		20
MAH-EEA ⁶⁾				20	
magnesium hydroxide ⁷⁾	40	90	100	120	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	2	4	4	2	2
total	143	195	205	223	133
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

35

Table 3

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
HDPE ¹⁾	100		20		
LLDPE ²⁾				30	
EVA ³⁾		100		70	50
PP ¹⁰⁾					
MAH-EVA ⁵⁾			80		50
MAH-PP ¹¹⁾					
magnesium hydroxide ⁷⁾	100	80	50	100	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	2	2	2	2
total	205	183	153	203	133

Table 3 (continued)

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
5	flexibility	failed	passed	passed	passed
	wear resistance	passed	failed	failed	failed
10	flame retardant quality	passed	passed	passed	passed
	formability	failed	passed	passed	passed

Table 4

	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9
15	HDPE 1)	65	60	85
20	EEDPE ²⁾			
	EVA ³⁾	10	10	25
25	PP 10)	30		
	MAH-EVA ⁵⁾	5	5	5
30	MAH-PP ¹¹⁾		30	
	magnesium hydroxide ⁷⁾	30	200	10
35	anti-aging agent ⁸⁾	1	1	1
	cross-linking adjuvant agent ⁹⁾	2	4	2
40	total	133	305	112
	flexibility	failed	failed	passed
	wear resistance	passed	passed	passed
	flame retardant quality	passed	passed	failed
45	formability	failed	failed	passed

1) high density polyethylene "HY331" manufactured by Japan Polychem Co., Ltd..
(MFR: 1.0g/ 10 min (JIS K 6760); density: 0.950).

2) straight-chain low density polyethylene "DFDJ 7540" manufactured by Japan Unika Co., LTD..
(MFR: 0.7 g/10min (JIS K 6760); density: 0.92).

3) ethylene-vinyl acetate copolymer "EV 360" manufactured by Mitsui Dupont Co., Ltd..

4) ethylene-ethyl acrylate copolymer "A 714" manufactured by Mitsui Dupont Co., Ltd..

5) maleic anhydride modified ethylene-vinyl acetate copolymer "VR-103" manufactured by Mitsui Dupont Co., Ltd..

6) maleic anhydride modified ethylene-ethyl acrylate copolymer "AR-201" manufactured by Mitsui Dupont Co., Ltd..

7) KISUMA 5 manufactured by Kyowa Chemicals Co., Ltd..

8) Hindered phenol type anti oxidant "Tominox TT" manufactured by Yoshitomi Pharmaceuticals Co. Ltd.

9) TMPT manufactured by New Nakamura Chemicals Co. Ltd;

10) polypropylene "RB610A" manufactured by Tokuyama Co., Ltd..

11) maleic anhydride modified polypropylene "ER 320P" manufactured by Japan Polyolefin Co., Ltd..

[0064] From the results of Comparative Examples 1 to 5, it can be understood that, when the amount of any one component chosen among components (a), (b1) and (c1) is outside the range defined in the present invention, at least one of the tested physical properties is not satisfied.

[0065] The results of Comparative Examples 6 and 7 show that, when any one of component (b1) and component (c1) is not used, the flexibility and formability of the composition deteriorate.

[0066] The results of Comparative Examples 8 and 9 indicate that, when the amount of magnesium hydroxide, a flame retardant (d) is too small, the flame retardant quality of the composition deteriorates. Conversely, when this amount is too large, the flexibility and formability of the composition deteriorate.

5 Examples 11 to 20 and Comparative Examples 10 to 18

[0067] The components shown in Tables 5 to 8 were used in the amounts indicated therein (parts by mass). Coated electrical cables were produced through the methods described for Examples 1 to 10, and the properties of the obtained coating were evaluated. The results thus obtained are given in Tables 5 to 8.

Table 5

	Example 11	Example 12	Example 13	Example 14	Example 15
HDPE 1)	60	50	65	30	50
LLDPE 2)					
EVA 3)	35	10		65	30
EEA 4)			5		
MAH-SEBS 12)	5	40	30	5	20
MAH-PP 11)					
magnesium hydroxide ⁷⁾	120	100	100	250	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	2	4	2
total	225	205	203	355	133
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 6

	Example 16	Example 17	Example 18	Example 19	Example 20
HDPE 1)		50	50	70	60
LLDPE 2)	90				
EVA 3)	5	30		10	20
EEA 4)			30		
MAH-SEBS 12)	5	20	20	20	20
MAH-PP 11)					
magnesium hydroxide ⁷⁾	50	90	100	120	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	4	4	4
total	155	195	205	225	135
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 7

	Comparative Example 10	Comparative Example 11	Comparative Example 12	Comparative Example 13	Comparative Example 14
HDPE 1)	100		20		
LLDPE 2)				20	
EVA 3)		100		80	50
PP 10)					
MAH-SEBS 12)			80		50
MAH-PP 11)					
magnesium hydroxide ⁷⁾	90	100	80	100	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	2	4	4	4
total	195	203	185	205	135
flexibility	failed	passed	passed	passed	passed
wear resistance	passed	failed	failed	failed	failed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 8

	Comparative Example 15	Comparative Example 16	Comparative Example 17	Comparative Example 18
HDPE 1)	55	60	75	80
LLDPE 2)				
EVA 3)		10	5	10
PP 10)	40			
MAH-SEBS 12)	5		20	20
MAH-PP 11)		30		
magnesium hydroxide ⁷⁾	30	180	10	300
anti-aging agent ⁸⁾	1	1	1	1
cross-linking adjuvant agent ⁹⁾	2	2	4	4
total	133	283	115	405
flexibility	failed	failed	passed	failed

Remarks in Tables 5 to 8:

Footnotes 1) to 4) and 7) to 11): see the footnotes for Tables 1 to 4.

12) maleic anhydride modified, hydrogenated styrene-butadiene block copolymer "Tuftec™ M1913" manufactured by Asahi Chemicals Co., Ltd..

Table 8 (continued)

	Comparative Example 15	Comparative Example 16	Comparative Example 17	Comparative Example 18
wear resistance	passed	passed	passed	passed
flame retardant quality	passed	passed	failed	passed
formability	failed	failed	passed	failed

[0068] From the results of Comparative Examples 10 to 14, it can be understood that, when the amount of any one component chosen among component (a), (b1) and (c2) is outside the range defined in the present invention, at least one of the physical properties tested is not satisfied.

[0069] The results of Comparative Example 15 show that, when an olefin polymer (b1) containing intra molecular oxygen atoms is not used, the flexibility and formability of the composition deteriorate.

[0070] The results of Comparative Example 16 indicate that, when an acid modified styrene type thermoplastic elastomer (c2) is not used, the flexibility and formability of the composition are lowered.

[0071] The results of Comparative Examples 17 and 18 show that, when the amount of magnesium hydroxide, a flame retardant (d), is too small, the flame retardant quality of the composition is poor. Conversely, when this amount is too large, the flexibility and formability of the composition deteriorate.

Examples 21 to 30 and Comparative Examples 19 to 27

[0072] The components shown in Tables 9 to 12 were used in the amounts (parts by mass) indicated therein, and coated electrical cables were produced according to the methods mentioned for Examples 1 to 10. The properties of the coatings obtained were then evaluated. The results are shown in Tables 9 to 12.

Table 9

	Example 21	Example 22	Example 23	Example 24	Example 25
HDPE 1)	65	50	65	30	50
LLDPE 2)					
EVA 3)	30	10	5		30
EEA 4)				65	
MAH-VLDPE 13)	5	40	30	5	20
MAH-PP 11)					
magnesium hydroxide ⁷⁾	110	100	120	250	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	2	4	4	4	
total	213	205	225	355	131
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 10

	Example 26	Example 27	Example 28	Example 29	Example 30
HDPE 1)		50	50	70	40
LLDPE 2)	90				

Table 10 (continued)

	Example 26	Example 27	Example 28	Example 29	Example 30
EVA 3)	5	30		10	40
EEA 4)			30		
MAH-VLDPE 13)	5	20	20	20	20
MAH-PP 11)					
magnesium hydroxide ⁷⁾	40	90	120	100	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	4	4	2
total	145	195	225	205	133
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 11

	Comparative Example 19	Comparative Example 20	Comparative Example 21	Comparative Example 22	Comparative Example 23
HDPE 1)	100		10		
LLDPE 2)				30	
EVA 3)		100		70	50
PP 10)					
MAH-VLDPE 13)			90		50
MAH-PP 11)					
magnesium hydroxide 7)	100	80	40	100	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	2	4	2	2
total	205	183	145	203	133
flexibility	failed	passed	passed	passed	passed
wear resistance	passed	failed	failed	failed	failed
flame retardant quality	passed	passed	passed	passed	passed
formability	failed	passed	passed	passed	passed

Table 12

	Comparative Example 24	Comparative Example 25	Comparative Example 26	Comparative Example 27
HDPE 1)	55	60	85	70

Table 12 (continued)

	Comparative Example 24	Comparative Example 25	Comparative Example 26	Comparative Example 27
5 LLDPE 2)				
EVA 3)		10	10	25
PP 10)	40			
10 MAH-VLDPE 13)	5		5	5
MAH-PP 11)		30		
magnesium hydroxide 7)	50	200	10	300
15 anti-aging agent 8)	1	1	1	1
cross-linking adjuvant agent 8)	4	4	4	2
total	135	305	112	403
20 flexibility	failed	failed	passed	failed
wear resistance	passed	passed	passed	passed
flame retardant quality	passed	passed	failed	passed
25 formability	failed	failed	passed	failed

Remarks :in Tables 9 to 12 :

Footnotes 1) to 4) and 7) to 11): see the footnotes for Tables 1 to 4.

13) maleic anhydride modified ultra-low density polyethylene "XE070" manufactured by Mitsui Chemicals Co., Ltd..(density: 0.893)

30 [0073] The results of Comparative Examples 19 to 23 show that, when the amount of any one component chosen among components (a), (b1) and (c3) is outside the range defined in the present invention, at least one of the properties tested is not satisfied.

[0074] The results of Comparative Example 24 indicate that, when an olefin polymer (b1) containing intra-molecular oxygen atoms is not used, the flexibility and formability of the composition are poor.

[0075] The results of Comparative Example 25 show that, when an acid modified styrene type thermoplastic elastomer (c3) is not used, the flexibility and formability of the composition are poor.

[0076] From the results of Comparative Examples 26 and 27, it can be understood that, when the amount of magnesium hydroxide, flame retardant as component (d), is too small, the flame retardant quality of the composition is poor. Conversely, when this amount is too large, the flexibility and formability of the composition deteriorate.

Examples 31 to 40 and Comparative Examples 28 to 36

45 [0077] The components shown in Tables 13 to 16 were used in the amounts (parts by mass), to produce coated electrical cables according to the methods described for Examples 1 to 10. The properties of the coatings were then evaluated. The results are shown in Tables 13 to 16.

Table 13

	Example 31	Example 32	Example 33	Example 34	Example 35
50 HDPE 1)	65	50	65	30	50
LLDPE 2)					
EVA 3)	30	10	5		30
EEA 4)				65	
55 MAH-EPM 14)	5	40	30	5	
MAH-EPDM 15)					20

Table 13 (continued)

	Example 31	Example 32	Example 33	Example 34	Example 35
magnesium hydroxide ⁷⁾	100	120	120	250	30
anti-aging agent ⁸⁾	1	1	2	1	1
cross-linking adjuvant agent ⁹⁾	4	4	2	4	4
total	205	225	224	355	135
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 14

	Example 36	Example 37	Example 38	Example 39	Example 40
HDPE ¹⁾		50	50	70	40
LLDPE ²⁾	90				
EVA ³⁾	5	30		10	40
EEA ⁴⁾			30		
MAH-EPM ¹⁴⁾	5	20	20	20	
MAH-EPDM ¹⁵⁾					20
magnesium hydroxide ⁷⁾	40	90	120	100	90
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	4	4	2
total	145	195	225	205	193
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 15

	Comparative Example 28	Comparative Example 29	Comparative Example 30	Comparative Example 31	Comparative Example 32
HDPE ¹⁾	100		10		
LLDPE ²⁾				30	
EVA ³⁾		100		70	50
PP ¹⁰⁾					
MAH-EPM ¹⁴⁾			90		50
MAH-PP ¹¹⁾					
magnesium hydroxide ⁷⁾	100	80	60	100	30

Table 15 (continued)

	Comparative Example 28	Comparative Example 29	Comparative Example 30	Comparative Example 31	Comparative Example 32
5 anti-aging agent ⁸⁾	1	1	1	1	1
10 cross-linking adjuvant agent ⁹⁾	4	2	4	2	2
15 total	205	183	165	203	133
20 flexibility	failed	passed	passed	passed	passed
wear resistance	passed	failed	failed	failed	failed
flame retardant quality	passed	passed	passed	passed	passed
formability	failed	passed	passed	passed	passed

Table 16

	Comparative Example 33	Comparative Example 34	Comparative Example 35	Comparative Example 36
25 HDPE ¹⁾	55	60	85	70
30 LLDPE ²⁾				
EVA ³⁾		10	10	25
35 PP ¹⁰⁾	40			
MAH-VLDPE ¹³⁾	5		5	5
40 MAH-PP ¹¹⁾		30		
magnesium hydroxide ⁷⁾	50	180	10	300
45 anti-aging agent ⁸⁾	1	1	1	1
cross-linking adjuvant agent ⁹⁾	2	4	2	2
total	133	285	112	403
flexibility	failed	failed	passed	failed
wear resistance	passed	passed	passed	passed
flame retardant quality	passed	passed	failed	passed
formability	failed	failed	passed	failed

50 [0078] Remarks in Tables 13 to 16 :

Footnotes 1) to 4) and 7) to 11): refer to the footnotes for Tables 1 to 4.

14) maleic anhydride modified ethylene-propylene copolymer rubber "T7741P" manufactured by JSR Co., Ltd..

15) maleic anhydride (2% grafted) modified ethylene-propylenediene copolymer rubber

55 [0079] The results of Comparative Examples 28 to 32 suggest that, when the amount of any one component chosen among components (a), (b1) and (c4) is outside the range defined in the present invention, at least one of the properties evaluated is not satisfied.

[0080] The results of Comparative Example 33 show that, when an olefin polymer (b1) containing intra-molecular

oxygen atoms is not used, the flexibility and formability of the composition are poor.

[0081] The results of Comparative Example 34 indicate that, when an acid modified rubber (c4) is not used, the flexibility and formability of the composition are poor.

[0082] The results of Comparative Examples 35 and 36 show that, when the amount of magnesium hydroxide, which is a flame retardant (component (d)), is too small, the flame retardant quality of the composition is poor. However, when this amount is too large, the flexibility and formability of the composition are deteriorated.

Examples 41 to 50 and Comparative Examples 37 to 45

[0083] The components shown in Tables 17 to 20 were used in the amounts (parts by mass), to produce coated electrical cables according to the methods described for Examples 1 to 10. The properties of the coatings were then evaluated. The results are shown in Tables 17 to 20.

Table 17

	Example 41	Example 42	Example 43	Example 44	Example 45
HDPE 1)	65	50	65	30	50
LLDPE 2)					
SEBS ¹⁶⁾	30	10		65	30
SEPS ¹⁷⁾			5		
MAH-SEBS ¹²⁾	5	40	30	5	20
MAH-PP ¹¹⁾					
magnesium hydroxide ⁷⁾	90	100	90	250	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	4	4	4	2	2
total	195	205	195	353	133
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 18

	Example 46	Example 47	Example 48	Example 49	Example 50
HDPE 1)		50	50	70	60
LLDPE 2)	90				
SEBS ¹⁶⁾	5	30		10	20
SEPS ¹⁷⁾			30		
MAH-SEBS ¹²⁾	5	20	20	20	20
MAH-PP ¹¹⁾					
magnesium hydroxide ⁷⁾	40	120	90	100	30
anti-aging agent ⁸⁾	1	1	1	1	1
cross-linking adjuvant agent ⁹⁾	2	2	4	4	4
total	153	223	195	205	135
flexibility	passed	passed	passed	passed	passed
wear resistance	passed	passed	passed	passed	passed

Table 18 (continued)

	Example 46	Example 47	Example 48	Example 49	Example 50
flame retardant quality	passed	passed	passed	passed	passed
formability	passed	passed	passed	passed	passed

Table 19

	Comparative Example 37	Comparative Example 38	Comparative Example 39	Comparative Example 40	Comparative Example 41
HDPE 1)	100		20		
LLDPE 2)				20	
SEBS 16)		100		80	70
PP 10)					
MAH-SEBS 12)			80		30
MAH-PP 11)					
magnesium hydroxide 7)	90	120	80	100	30
anti-aging agent 8)	1	1	1	1	1
cross-linking adjuvant agent 9)	4	2	4	4	4
total	195	223	185	205	135
flexibility	failed	passed	passed	passed	passed
wear resistance	passed	failed	failed	failed	failed
flame retardant quality	passed	passed	passed	passed	passed
formability	failed	passed	passed	passed	passed

Table 20

	Comparative Example 42	Comparative Example 43	Comparative Example 44	Comparative Example 45
HDPE 1)	55	60	85	80
LLDPE 2)				
SEBS 16)		10	5	10
PP 10)	40			
MAH-SEBS 12)	5		10	10
MAH-PP 11)		30		
magnesium hydroxide 7)	30	200	10	300
anti-aging agent 8)	1	1	1	1
cross-linking adjuvant agent 9)	2	4	4	4

Table 20 (continued)

	Comparative Example 42	Comparative Example 43	Comparative Example 44	Comparative Example 45	
5	total	133	305	115	405
	flexibility	failed	failed	passed	failed
10	wear resistance	passed	passed	passed	passed
	flame retardant quality	passed	passed	failed	passed
	formability	failed	failed	passed	failed

[0084] Remarks in Tables 17 to 20 :

Footnotes 1)to 4) and 7) to 11): see the footnotes for Tables 1 to 4.

12) see the footnotes for Tables 5 to 8 .

16)' hydrogenated styrene-butadiene block copolymer manufactured by Asahi chemicals Co., Ltd..

17) hydrogenated styrene-ethylene-propylene block copolymer manufactured by Kurare Co., Ltd..

[0085] From the results of Comparative Examples 37 to 41, it can be understood that, when the amount of any one component chosen among components (a), (b2) and (c2) is outside the range defined in the present invention, at least one of the physical properties evaluated is not sufficient.

[0086] The results of Comparative Example 42 indicate that, when an olefin polymer (b2) containing intra-molecular oxygen atoms is not used, the flexibility and formability of the composition are not sufficient.

[0087] The results of Comparative Example 43 show that, when an acid modified styrene type thermoplastic elastomer (c2) is not used, the flexibility and formability of the composition are poor.

[0088] The results of Comparative Examples 44 and 45 suggest that, when the amount of magnesium hydroxide, which is a flame retardant (component (d)), is too small, the flame retardant quality of the composition is poor. However, when this amount is too large, the flexibility and formability of the composition are poor.

30 Examples 51 to 60 and Comparative Examples 46 to 54

[0089] The components shown in Tables 21 to 24 were used in the amounts (parts by mass), to produce coated electricalcables according to the methods described for Examples 1 to 10. The properties of the coatings were then evaluated. The results are shown in Tables 21 to 24.

Table 21

	Example 51	Example 52	Example 53	Example 54	Example 55	
40	HDPE 1)	65	50	60	30	50
	LLDPE 2)					
45	SEES 16)	30	10		65	30
	SEPS 17)			5		
	MAH-EVA 5)					
50	MAH-EEA 6)	5	40	35	5	30
	magnesium hydroxide 7)	90	100	100	250	30
55	anti-aging agent 8)	1	1	1	1	1
	cross-linking adjuvant agent 9)	4	4	2	4	4
	total	195	205	203	355	135
	flexibility	passed	passed	passed	passed	passed
	wear resistance	passed	passed	passed	passed	passed
	flame retardant quality	passed	passed	passed	passed	passed
	formability	passed	passed	passed	passed	passed

Table 22

		Example 56	Example 57	Example 58	Example 59	Example 60
5	HDPE 1)		50	50	70	60
10	LLDPE 2)	90				
15	SEBS 16)		30	20		
20	SEPS 17)	5			10	20
25	MAH-EVA 5)	5	20		20	
	MAH-EEA 6)			30		20
	magnesium hydroxide 7)	70	120	100	120	30
	anti-aging agent 8)	1	1	1	1	1
	cross-linking adjuvant agent 9)	4	4	4	4	4
	total	175	225	205	225	135
	flexibility	passed	passed	passed	passed	passed
	wear resistance	passed	passed	passed	passed	passed
	flame retardant quality	passed	passed	passed	passed	passed
	formability	passed	passed	passed	passed	passed

Table 23

	Comparative Example 46	Comparative Example 47	Comparative Example 48	Comparative Example 49	Comparative Example 50
30	HDPE 1)	100		20	
35	LLDPE 2)			20	
40	SEBS 16)		100		80
45	PP 10)				
50	MAH-EVA 5)			80	50
55	MAH-PP 11)				
	magnesium hydroxide 7)	90	120	50	100
	anti-aging agent 8)	1	1	1	1
	cross-linking adjuvant agent 9)	4	2	2	4
	total	195	223	153	205
	flexibility	failed	passed	passed	passed
	wear resistance	passed	failed	failed	failed
	flame retardant quality	passed	passed	passed	passed
	formability	failed	passed	passed	passed

Table 24

	Comparative Example 51	Comparative Example 52	Comparative Example 53	Comparative Example 54
HDPE 1)	55	60	90	85
LLDPE 2)				
SEBS 16)		5	5	5
PP 10)	40			
MAH-EVA 5)	5		5	10
MAH-PP 11)		35		
magnesium hydroxide 7)	200	180	10	300
anti-aging agent 8)	1	1	1	1
cross-linking adjuvant agent 9)	2	2	4	4
total	303	283	115	405
flexibility	failed	failed	passed	failed
wear resistance	passed	passed	passed	passed
flame retardant quality	passed	passed	failed	passed
formability	failed	failed	passed	failed

[0090] Remarks in Tables 21 to 24 :

Footnotes 1) to 4) and 7) to 11): see the footnotes for Tables 1 to 4.

Footnotes 16) and 17): see footnotes for Tables 17 to 20.

[0091] The results of Comparative Examples 46 to 50 indicate that, when the amount of any one component chosen among components (a), (b2) and (c1) is outside the range defined in the present invention, at least one of the properties evaluated is not satisfactory.

[0092] The results of Comparative Example 51 suggest that, when an olefin polymer (b2) containing intra-molecular oxygen atoms is not used, the flexibility and formability of the composition are poor.

[0093] The results of Comparative Example 52 show that, when an acid modified styrene type thermoplastic elastomer (c1) is not used, the flexibility and formability of the composition are poor.

[0094] The results of Comparative Examples 53 and 54 indicate that, when the amount of magnesium hydroxide, flame retardant component (d), is too small, the flame retardant quality of the composition is poor, whereas, when this amount is too large, the flexibility and formability of the composition are poor.

Claims

1. A resin composition comprising:

- (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b1) about 5 to 65 parts by mass of olefin type polymer containing intra molecular oxygen atoms;
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

(c1) acid modified olefin polymers containing intra-molecular oxygen atoms;

(c2) acid modified styrene type thermoplastic elastomers;

(c3) acid-modified polyethylenes having a density of about 0.920 at the most; and

(c4) acid modified rubbers,

with the proviso that the total of components (a), (b1) and (c) represents 100 parts by mass; and

- (d) about 30 to 250 parts by mass of metal hydroxide.

2. A resin composition comprising:

- 5 - (a) about 30 to 90 parts by mass of polyethylene having a melt flow rate (MFR) of about 5g/10 min at the most and a density of at least about 0.930;
- (b2) about 5 to 65 parts by mass of styrene type thermoplastic elastomer; and
- (c) about 5 to 40 parts by mass of at least one type of polymer selected from the group consisting of:

10 (c1) acid modified olefin type polymers containing intra-molecular oxygen atoms, and
(c2) acid modified styrene type thermoplastic elastomers;
with the proviso that the total of components (a), (b2) and (c) represents 100 parts by mass; and

- (d) about 30 to 250 parts by mass of metal hydroxide.

15 3. The resin composition according to claim 1 or 2, wherein said resin composition is cross-linked by electron beam irradiation.

20 4. A method for preparing an electrical cable, said method comprising the steps of:

- preparing a resin composition defined in any one of claims 1 to 3; and
- coating a conductor element with said resin composition.

25 5. The method according to claim 4, further comprising the step of irradiating said resin composition with electron beams.

6. An electrical cable coated with a resin composition defined in any one of claims 1 to 3.

30 7. The use of a resin composition defined in any one of claims 1 to 3 for preparing an electrical cable.

35

40

45

50

55